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(54) **Automatic sample supply**

(57) A mechanism for automatically supplying sample liquids to a chromatographic column comprises a turntable 11 carrying sample vessels 12 and a dosing tube 20, the lower end of which is movable between a take-up point 14 where the end is immersed in a vessel 12 on the turntable 11 and a discharge point 36 at which the lower end is connected via a change-over valve 38 to one end of a measuring loop 42. In operation a quantity of sample liquid is sucked into the tube 20 by a dosing pump 34. The tube 20 is then moved to the discharge point and the discharge stroke of the pump 34 forces the sample into the measuring loop 42. The valve 38 is then moved to its alternative position in which ports 54 and 56 are connected by a conduit 70 and ports 40 and 58 are connected by a conduit 68. A solvent pump is connected to the port 56 and the chromatographic column is connected to the port 40 and the resultant solvent flow thus forces the sample in the measuring loop 42 into the column.

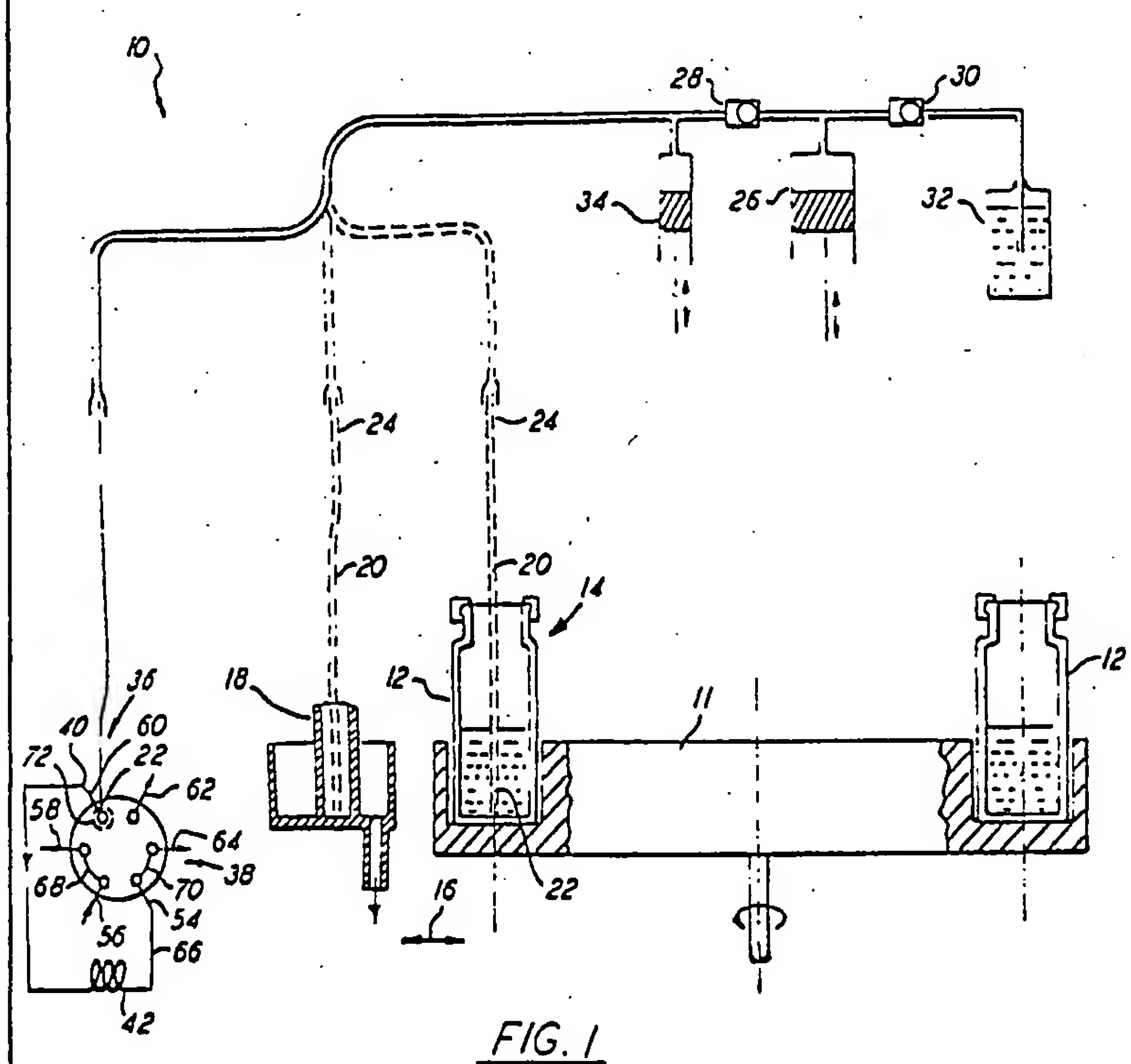

FIG. 1

The drawing(s) originally filed was/were informal and the print here reproduced is taken from a later filed formal copy.

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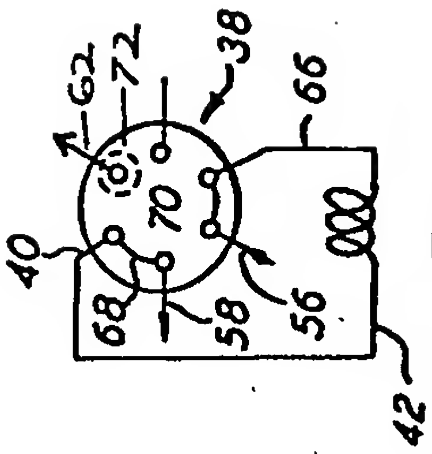


FIG. 2

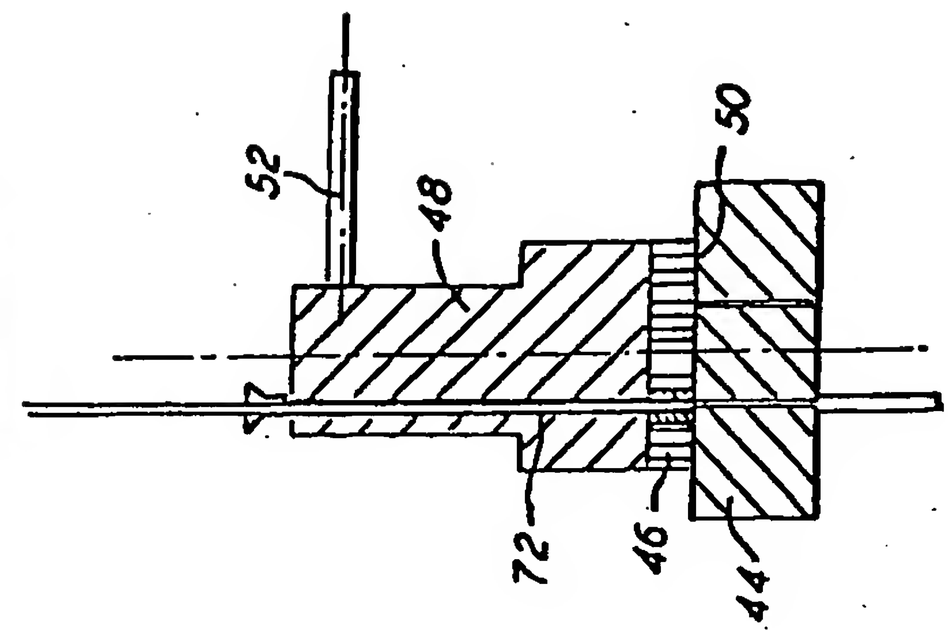


FIG. 3

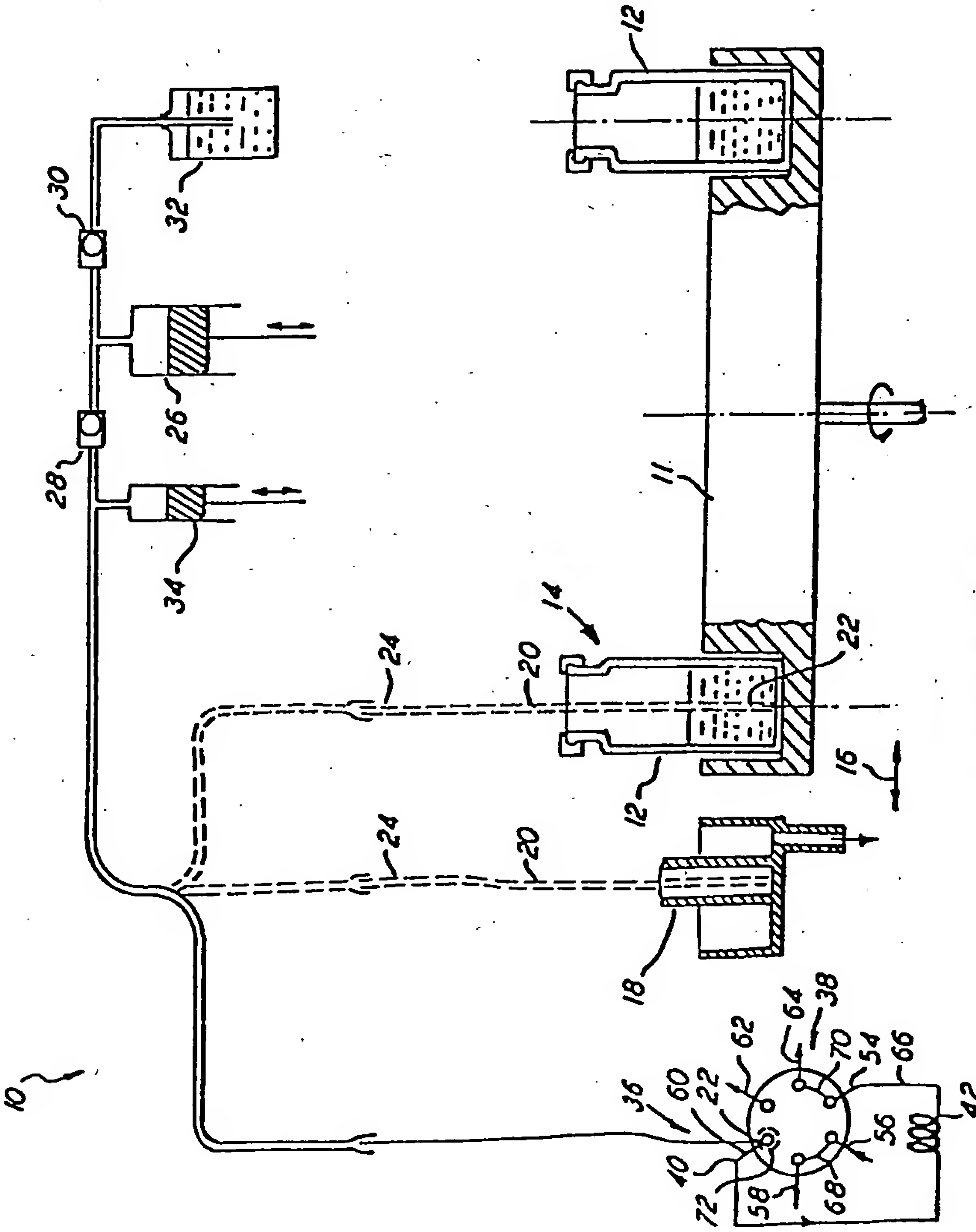
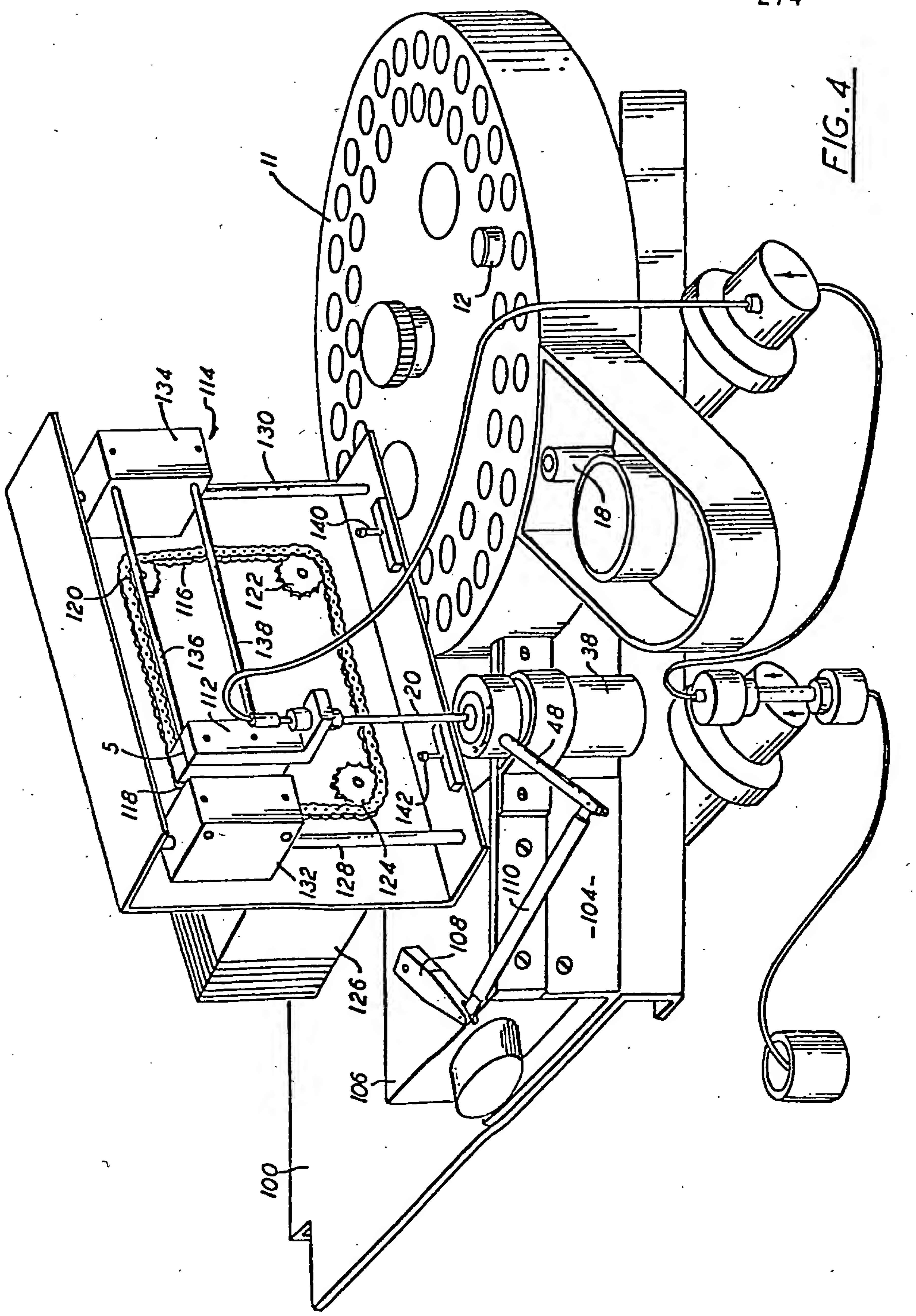


FIG. 1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-104-
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106
100

FIG. 4

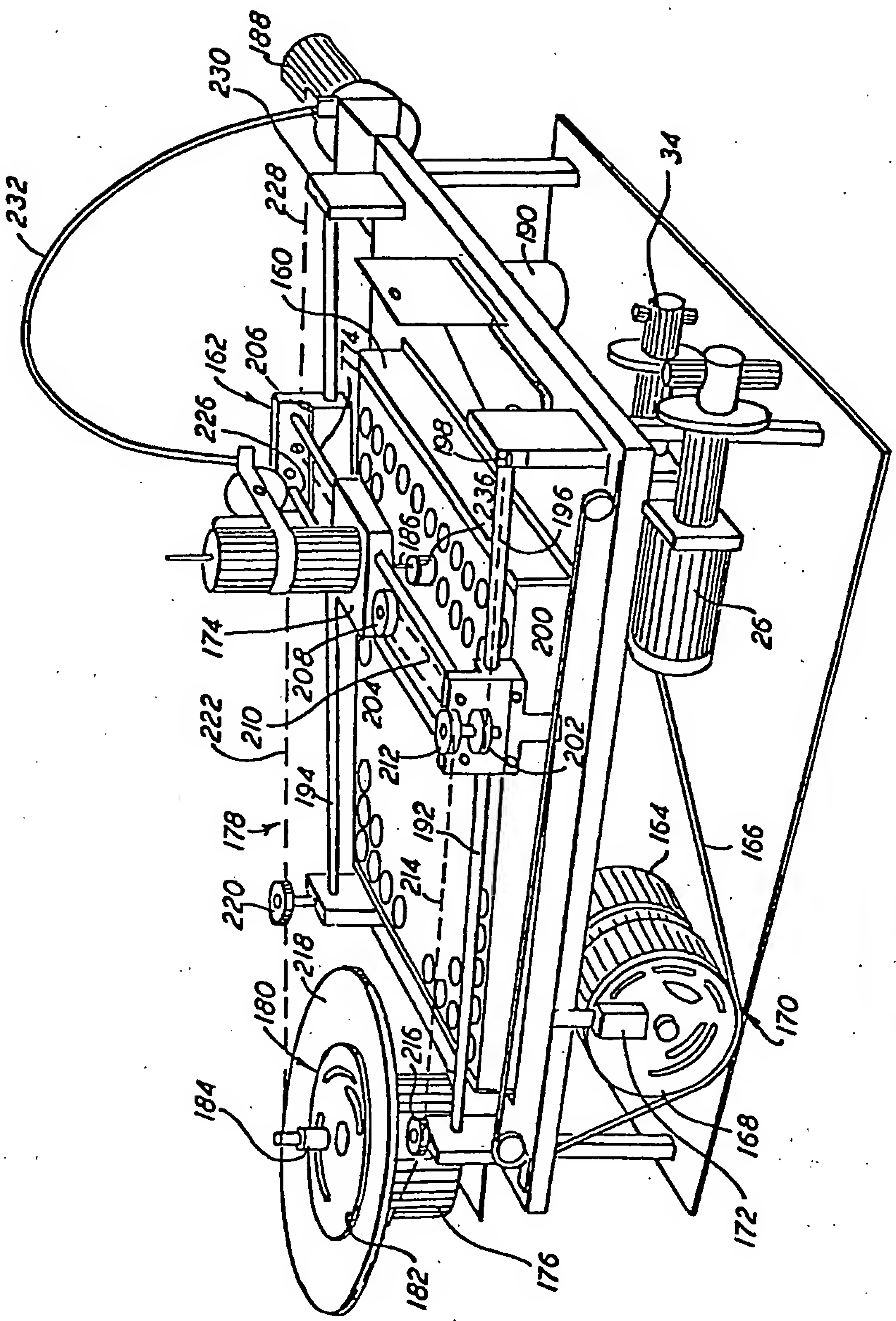
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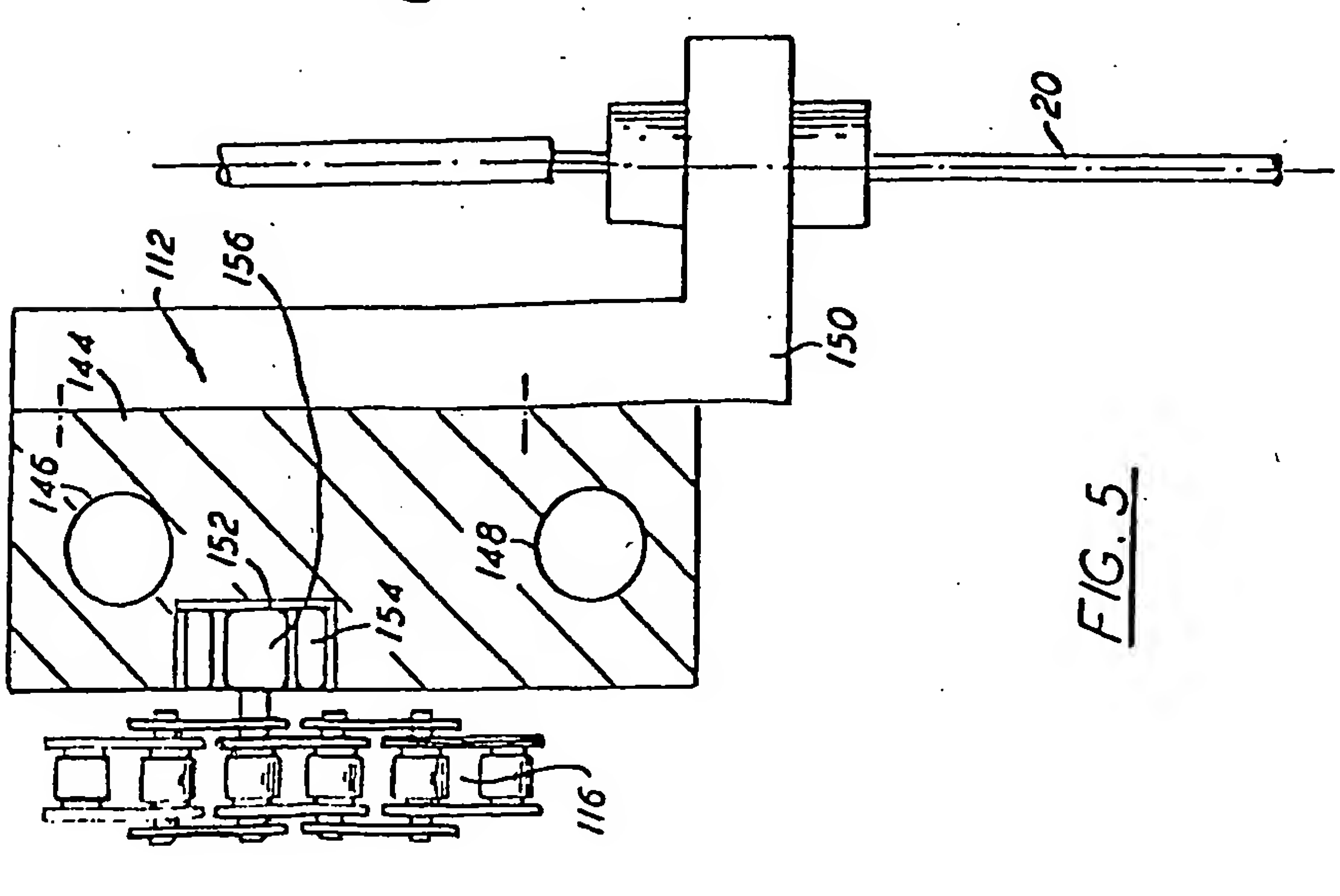
FIG. 7


20
112
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144
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FIG. 5

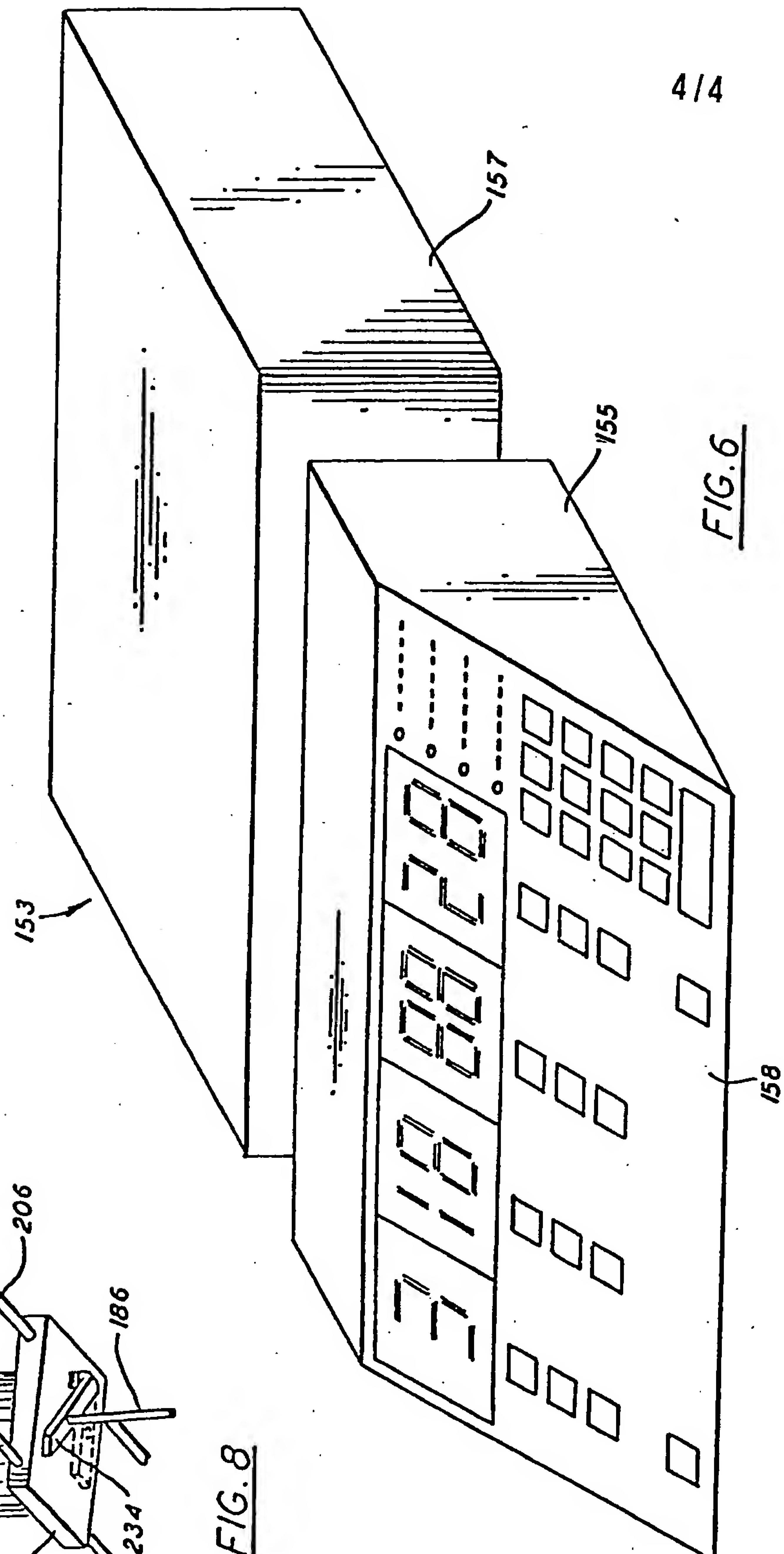

FIG. 6

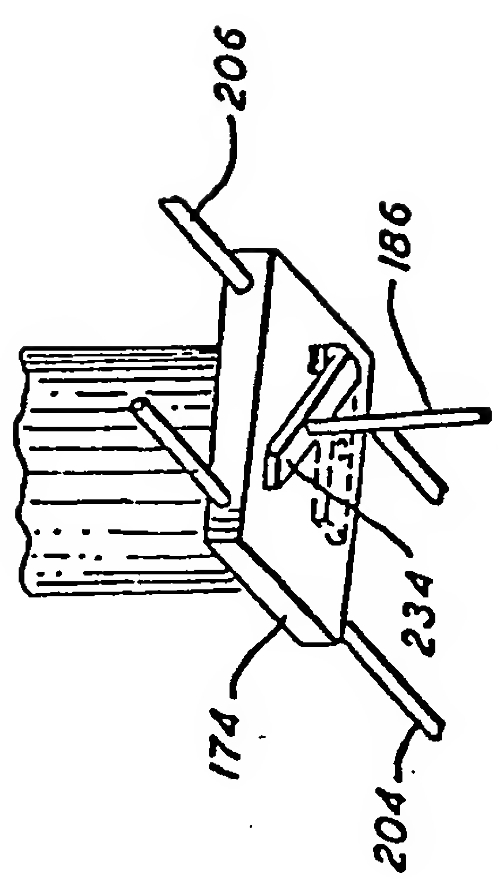

FIG. 8

SPECIFICATION

Automatic sample supply

This invention relates generally to a mechanism for automatically supplying samples for analytical purposes, and, in particular, relates to such a mechanism for supplying a liquid sample to the measuring loop of a liquid chromatograph.

A liquid chromatograph comprises a separating column, through which a solvent is pumped. A liquid sample to be tested is inserted into this solvent flow and interacts with a separating substance present in the separating column. The sample substances are transported by the solvent flowing through the separating column with different transporting speeds depending on the strength of the interaction between the separating substance and the sample substance. Consequently, the components of the sample emerge successively from the exit of the separating column and can be captured individually, for example, by means of a fractional collector. The quantity of sample is supplied into the solvent fluid by means of a "measuring loop". The measuring loop is often a length of tube connected between a solvent pump and the entrance of the separating column, whereby the solvent flow through the tube carries the sample contained therein into the separating column.

According to the present invention mechanism for automatically supplying liquid samples from sample vessels to a measuring loop of a liquid chromatographic column comprises a dosing tube, a change-over valve having a number of ports, a measuring loop connected between a first and second port of the change-over valve, a solvent pump outlet connected to a third port of the change-over valve, means for positioning the dosing tube alternatively in first and second positions in the first of which the front end of the dosing tube is in one of the sample vessels and its rear end communicates with a dosing pump whereby sample liquid is sucked into the dosing tube and in the second of which the front end communicates with the first port of the change-over valve and the dosing pump discharges the sample from the dosing tube into the measuring loop, and a control unit for controlling and synchronising the operation of the change-over valve with the dosing tube position in such a way that when the dosing tube is in its first position the solvent pump communicates with the column and when the dosing tube is in its second position the solvent pump communicates with the column via the measuring loop.

Examples of mechanism in accordance with the invention will now be described in more detail with reference to the accompanying drawings, in which:-

Figure 1 is a diagrammatic representation of apparatus in accordance with the invention;

Figure 2 is a detailed view of a change-over valve forming part of the apparatus shown in Figure 1, the valve being in a second position;

Figure 3 is a sectional view of the portion of the apparatus shown in Figure 2;

Figure 4 is a perspective view of another form of apparatus in accordance with the invention;

Figure 5 is a cross sectional view of a portion of the apparatus shown in Figure 4, taken along the line 5 - 5 in Figure 4;

Figure 6 is a perspective view of a control unit for the apparatus;

Figure 7 is a perspective view of another form of apparatus in accordance with the invention; and

Figure 8 shows a detail of the apparatus shown in Figure 7.

Turning first to Figure 1, apparatus generally designated as 10 includes a turntable 11 forming a transport mechanism for sample vessels 12, which are successively transported to a sample take-up station 14. The turntable 11 is located on a support (not illustrated in Figure 1) which is movable between first and second positions, as indicated by the arrow 16. A washing vessel 18, formed as an overflow vessel, is positioned on the support next to the turntable 11. In one position a sample vessel 12 is at the sample take-up station below a dosing tube 20. In another position the washing vessel 18 is so located below the dosing tube 20. The lower or front end 22 of the dosing tube 20 can be selectively immersed in either the sample vessel 12 or the washing vessel 18, depending upon the position of the support.

The upper or rear end 24 of the dosing tube 20 is connected via a washing liquid pump 26 and associated check valves 28 and 30 to a washing liquid vessel 32. In addition, the upper end 24 of the dosing tube 20 is connected to a dosing pump 34, which selectively sucks in and discharges a predetermined quantity of sample liquid.

The dosing tube 20 is movable, in a manner more fully described below, between the sample take-up station 14, at which station its free lower end 22 is immersed in a sample vessel 12 and a sample discharge station 36, at which station the lower end 22 of the dosing tube 20 is connected, via a change-over valve 38, to one end 40 of a measuring loop 42.

As illustrated, the change-over valve 38 is a rotary slide valve, including a stator 44 and a rotor 48 engaging the stator 44 with a sealing disc 46 (see Figure 3). The stator 44 and rotor 48 engage each other in a plane valving surface 50. The rotor 48 is rotatable between the first and second positions by means of a lever 52.

In Figure 1, the change-over valve 38 is shown in its first position. In the illustrated embodiment, the stator 44 has six ports 54, 56, 58, 60, 62 and 64 angularly spaced from each other by 60°. Two of the ports, 54 and 60 are diametrically opposite each other and are connected to the two ends, 40 and 66 respectively of the measuring loop 42. A further two ports 62 and 64, located between the two ports 54 and 66 are connected to outlets. One of the remaining ports 56 is connected to a solvent pump (not shown) and the sixth port 58 is connected to the chromatographic column (not shown). The rotor 48 further includes, in its control surface and packing disc 46, two connecting conduits 68 and 70 each extending through 60° and angularly spaced from each other by 60°. At the sample discharge station 36

the free end 22 of the dosing tube is adapted to be connected to a port 72 of the rotor 48, which port opens into the valving surface 50 and which is angularly spaced from one of the connecting conduits by 60°.

In the position illustrated in Figure 1, the entrance of the chromatographic column is connected via the connecting conduit 68 to the solvent pump. One end 40 of the measuring loop 42 is connected to the free end 22 of the dosing tube 20, whereas the other end 66 of the measuring loop 42 is connected through the connecting conduit 70 to the outlet. With a discharge stroke of the dosing pump 34 a quantity of liquid sample sucked into the dosing tube 20 is forced into the measuring loop 42 to displace the solvent present therein to the outlet. The measuring loop 42 can be filled up with sample liquid, for which purpose a small excess of sample liquid may be sucked up and then delivered by the dosing pump. It is also possible; however, to force a quantity of sample liquid less than the volume of the measuring loop 42 into the loop.

In the second position of the change-over valve 38, shown in Figure 2, the free end 22 of the dosing tube 20 is connected through the port 72 of the rotor 48 and the port 62 of the stator 44 to an outlet. The solvent pump connected to the port 56 of the stator 44 is connected through the connecting conduit 70 to the end 66 of the measuring loop 42. The other end 40 of the measuring loop is connected through the connecting conduit 68 of the rotor and the port 58 of the stator 44 to the chromatographic column. Thus the measuring loop 42 is connected between the solvent pump and the chromatographic column and the sample liquid quantity contained in the measuring loop 42 is transferred to the chromatographic column by the solvent flow.

The arrangement described above operates as follows:-

The movement of the dosing tube, the dosing pump 34, the washing liquid pump 26 and the turntable 11 are synchronously controlled by a control unit. After a fresh sample vessel 12 has reached the sample take-up station 14, the dosing tube 20 is moved horizontally over the sample vessel 12 and then vertically thereinto. In this position, the free end 22 of the dosing tube 20 is immersed in the sample liquid and a quantity of sample liquid is sucked into the dosing tube 20 by the dosing pump 34. The dosing tube 20 is then moved upwards and laterally to the sample discharge station 36 and pushed into the rotor 48 of the change-over valve 38, as illustrated schematically in Figure 1 and constructionally in Figure 3. The discharge stroke of the dosing pump 34 now takes place whereby the sample liquid previously sucked in is forced into the measuring loop 42. After changing over the change-over valve 38 to its second position by means of the lever 52, the sample liquid supplied to the measuring loop 42 is forced into the chromatographic column by the solvent flow.

The dosing tube 20 is then pulled upwards out of the rotor 48 of the change-over valve 38. The support (not shown in Figure 1) is moved into its second end position, so that the washing vessel 18 rather than the sample vessel 12 is at the sample take-up station 14 below the dosing tube 20. The dosing tube 20 is then immersed in the washing vessel 18. Washing liquid is pumped out of the washing liquid container 32 through the dosing tube 20 into the washing vessel 18 by the washing liquid pump 26. A sufficient quantity of washing liquid is delivered until the washing vessel 18 overflows. Thus, the free end of the dosing tube 20 is thoroughly cleaned on both the outside and the inside, of any residue of the previously delivered sample. The dosing tube 20 is then pulled out of washing vessel 18. The dosing pump 34 now sucks a small quantity of air into the dosing tube 20, which air serves as a pocket to separate the sample liquid subsequently sucked in from the washing liquid.

Simultaneously the turntable 11 is rotated, normally by one step. Thus when the support is returned to its first position, the next sample vessel 12 is at the sample take-up station 14. The dosing tube 20 is moved down again and its free end 22 is immersed in the sample liquid as described. The next sample is now sucked into the dosing tube 20 in the manner already described.

One particular advantageous constructional embodiment of the above described apparatus 10 is shown in Figure 4.

The turntable 11 is rotatably and pivotally mounted on a base plate 100. The turntable 11 includes, for example, forty spaces into which sample vessels 12 can be inserted. The washing vessel 18 is pivotable with the turntable 11. The turntable 11 with the projection comprising the washing vessel 18 forms the "support" mentioned above. The change-over valve 38 is mounted on the base plate 100 by means of a bracket 104. A pneumatic servomotor 106 is located on the same bracket 104 and has a pivoting lever 108 which is connected to the lever 48 of the valve 38 via a linkage 110.

The dosing tube 20 is attached to a dosing tube holder 112 in a vertical position. Means 114 are provided for holding the dosing tube holder 112 vertical while permitting both vertical and horizontal movement thereof. A driving chain 116 passes around four sprocket wheels 118, 120, 122 and 124 arranged at the corners of a rectangle having vertical and horizontal sides, one wheel of which is arranged to be driven by a servomotor 126. The dosing tube holder 112 is connected to the driving chain 116 as illustrated in Figure 5.

The holding means 114 includes a pair of vertical bars 128 and 130 laterally spaced from each other and a pair of blocks 132 and 134 which are guided on respective vertical bars 128 and 130. A pair of horizontal bars 136 and 138 are arranged between the blocks 132 and 134 and are vertically spaced from each other in a plane parallel to the plane of the vertical bars 128 and 130. The dosing tube holder 112 is guided to slide on these horizontal bars 136 and 138. The dosing tube holder 112 is guided to slide on these horizontal bars 136 and 138. The dosing tube holder 112 can thus move horizontally on the bars 136 and 138 which themselves can move vertically with the blocks 132 and 134. When the

driving chain 116 is caused to move, the dosing tube holder 112 thus moves horizontally or vertically along with the driving chain 116. In Figure 4, the sample take-up station is on the right and the sample discharge station is on the left. The dosing tube holder 112 with the dosing tube 20 moves horizontally between these two stations, the holder 112 moving vertically downwards upon reaching the respective station. The downward motion of the dosing tube holder 112 is limited by adjustable stops 140 and 142, respective, at the sample take-up station 14 and the discharge station 36.

As can be seen from Figure 5, the dosing tube holder 112 comprises a block 144 formed with two parallel bores 146 and 148 for the passage of the bars 136 and 138. A bracket 150 is provided on the block 144, to which bracket 150 the dosing tube 20 is retained at its upper end 24. The block 144 includes a recess 152 having a roller bearing 154 therein, which bearing 154 is connected via an elongated bolt 156 to the driving chain 116.

The operating sequence is determined by a control unit 153 which consists of two spaced-apart assemblies 155 and 157, one of which, 155, comprises the operation and display field 158 only and the other, 157, comprises a micro-processor and the associated interfaces. The fact that the two units are separate offers the practical advantage that the assembly 155 with the operation and display field 158 can be arranged at a distance from the liquid chromatograph and from the described arrangement for supplying the sample.

Figures 7 and 8 show a modified form of the mechanical construction. In the embodiment of Figures 7 and 8, the sample vessels are arranged in a stationary holder 160 of generally rectangular shape in parallel rows such that each sample vessel can be characterised by a row and a column number. In this embodiment, the holder 160 is stationary and the dosing tube 186 is moved relative thereto. To this end a cradle 162 extending parallel to the rows is movably guided above the holder 160 in a direction perpendicular to the rows. The cradle 162 is adjustable by a first servo motor 164 through a rope transmission 166. The position of the servomotor 164 is controlled by a first coding device 168, which, in one instance, consists of a coded disc 170 located on the shaft of the servomotor 164 and of a light barrier arrangement 172. A carriage 174 is movably guided on the cradle 162 along the rows, which carriage 174 is adjustable by a second servomotor 176 through a rope transmission 178. The position of the servomotor 176 can be controlled by a second coding device 180. The second coding device 180 consists of a code disc 182 and a light barrier arrangement 184. The dosing tube 186 is vertically movable by a third servomotor 188. The cradle 162 and the carriage 174 are movable to a position beside the holder 160, in which position the dosing tube 186 is located above the sample discharge station, where a valve 190 of the type of Figure 3 is arranged.

The second servomotor 176 is fixed to the apparatus on one side of the holder 160. The cradle 162 is guided on two parallel guiding bars 192 and 194. The rope transmission 178 controlled by the second servomotor 176 comprises a rope 196, which is fixed to the apparatus at one end 198 on the side remote from the servomotor 176. One length 200 of the rope 196 extends along one sliding bar 192 and changes direction around a first roller 202 at one side of the cradle 162. The rope 196 is then guided along the guide means of the carriage 174 which is formed by two sliding bars 204 and 206, passing next to a second roller 208 on the carriage 174. The rope 196 changes direction through 180° on passing round the second roller 208 and then passes round a further roller 212 after which a rope length 214 passes along the bar 192. The rope 196 then changes direction again around a roller 216 and is wound around a pulley 218 mounted on the servomotor 176.

After passing around the pulley 218, the rope 196 extends around a roller 220 and a length 222 passes along the other sliding bar 194. The rope 196 then passes (in a manner not illustrated but similar to that at the front in Figure 7) about a fourth roller provided on the other side on the cradle 162, is deflected by this roller and a length 224 is guided along the guide means 204 and 206 of the carriage 174 to a fifth deflecting roller (not visible) provided on the carriage 174. The rope 196 again changes direction through 180° around the fifth roller and a length 226 is guided to a co-axial sixth deflecting roller provided on the cradle 162. The rope is deflected thereby and a length 228 is guided along the other sliding bar 194 and fixed to the apparatus at the other end 230 on the side remote from the servomotor 176.

With such a rope transmission it is possible for the servomotor 176 to be fixed with respect to the apparatus. The cradle 162 can thus be moved along the sliding bars 192 and 194 by the servomotor 164 without affecting the position of the carriage 174 relative to the cradle 162. The carriage 174 is moved, again without affecting the position of the cradle 162, by the servomotor 176. Defined, discrete positions of the cradle 162 and the carriage 174 are predetermined by the coding devices 170 and 180 which positions correspond to a vessel in the holder 160. Thus, the dosing tube 186 together with the carriage 174 can be moved over each sample vessel in the holder 160.

The third servomotor 188 is also fixed with respect to the apparatus, the downward and upward motion being transmitted from this servomotor to the dosing tube 186 via, for example, a Bowden cable 232.

As illustrated in Figure 8, a device 234 is provided on the carriage 174, which device 234 holds down the sample vessel 236 into which the dosing tube is inserted, while the dosing tube 136 is retracted, if closed sample vessels 236 (Figure 7) covered by a septum are used. In order to prevent the device 234 from interfacing with the insertion of the dosing tube 186 into the changeover valve 190 at the sample discharge station, the device 234 is pivotably mounted. Thus at the sample discharge station the device 234 is automatically deflected into the position illustrated in dotted lines.

CLAIMS

1. Mechanism for automatically supplying liquid samples from sample vessels to a measuring loop of a liquid chromatographic column, the mechanism comprising a dosing tube, a change-over valve having a number of ports, a measuring loop connected between a first and second port of the change-over valve, a solvent pump outlet connected to a third port of the change-over valve, means for positioning the dosing tube alternatively in first and second positions in the first of which the front end of the dosing tube is in one of the sample vessels and its rear end communicates with a dosing pump whereby sample liquid is sucked into the dosing tube, and in the second of which the front end communicates with the first port of the change-over valve and the dosing pump discharges the sample from the dosing tube into the measuring loop, and a control unit for controlling and synchronising the operation of the change-over valve with the dosing tube position in such a way that when the dosing tube is in its first position the solvent pump communicates with the column and when the dosing tube is in its second position the solvent pump communicates with the column via the measuring loop.

2. Mechanism according to claim 1 and further comprising a washing liquid pump connected via an intake port to a washing liquid vessel and, via a discharge port, to the rear end of the dosing tube and the control unit operates to initiate a washing process after each sample intake, during which process the dosing tube is moved to an operational position over a washing vessel, the washing pump providing washing liquid from the washing liquid vessel through the dosing tube and into the washing vessel.

3. Mechanism according to claim 2 wherein the sample vessels are successively movable to a sample take-up station by a transport mechanism, both the transport mechanism and the washing vessel being arranged on a carrier movable between two positions in one of which a sample vessel is located at the sample take-up station below the dosing tube and in the other of which the washing vessel is moved to this position by means of the control unit.

4. Mechanism according to any one of the preceding claims wherein the change-over valve is a rotary slide valve including a stator and an engaging rotor with a plane valving surface, the stator having six ports angularly spaced from each other by 60°, of which two ports diametrically opposite each other are connected to the two ends of the measuring loop, two adjacent ports between the first two ports are connected to outlets, one of the other ports is connected to the solvent pump and the sixth port is connected to the chromatographic column, the rotor including in its valving surface two connecting conduits extending through 60° each and angularly spaced from each other by 60° and the free end of the dosing tube at the sample discharge station being arranged to be connected to a port of the rotor which port opens into the valving surface and which is angularly spaced from one of the connecting conduits by 60°.

5. Mechanism according to claim 4, wherein the rotor is movable by a servomotor between two positions angularly spaced from each other by 60°, so that in one position the port arranged to be connected to the dosing tube is aligned with a port of the stator, connecting to one end of the measuring loop and in the other position the said port of the stator communicates through one of the connecting conduits with the port of the stator connecting with the chromatographic column.

6. Mechanism according to any one of the preceding claims and including a dosing tube holder to which the dosing tube is vertically attached, means for holding the dosing tube holder in a fixed angular position while permitting vertical and horizontal movement, and a driving chain attached to the dosing tube holder and passing around four sprocket wheels arranged at the corners of a rectangle with vertical and horizontal sides, one wheel of which is arranged to be driven by a servomotor.

7. Mechanism according to claim 6 wherein means for holding the dosing tube holder in a fixed angular position includes a pair of laterally spaced blocks each guided on a respective vertical slide bar, a pair of vertically spaced horizontal slide bars extending between the blocks in a plane parallel to the plane of the vertical slide bars, the dosing tube holder being guided on the horizontal slide bars.

8. Mechanism according to any one of the preceding claims wherein downward motion of the dosing tube is limited by adjustable stops.

9. Mechanism according to any one of the preceding claims wherein the control unit includes two separate assemblies, one of which comprises only the operation and display field and the other one comprises a micro-processor and the associated interfaces.

10. Mechanism according to any one of the preceding claims wherein the sample vessels are arranged in parallel rows in a stationary holder such that each sample vessel is characterised by a row and column number, a cradle extending parallel to the rows is movably guided above the holder in a direction perpendicular to the rows under the control of a first servomotor through a rope transmission, the position of the servomotor being controlled by a first coding device, a carriage is movably guided on the cradle in a direction along the rows, which carriage is adjustable by a second servomotor through a rope transmission, the position of the servomotor being controlled by a second coding device, the dosing tube being vertically movable by a third servomotor and the cradle and the carriage are movable into a position beside the sampling vessel holder, at which position said dosing tube is located above the sample discharge station.

11. Mechanism according to claim 10 wherein the second servomotor is fixed with respect to the apparatus on one side of the holder, the cradle is guided on two parallel slide bars and the rope transmission connected to the second servomotor comprises a rope which is fixed to the apparatus at one end on the side remote from the servomotor, extends along one slide bar for the cradle, is

deflected around a first roller provided on one side of the cradle and which is guided aong the guide means of the carriage to a second deflecting roller provided thereon, is deflected through 180° by the second deflecting roller and is guided to and deflected by a third deflecting roller provided on the cradle and co-axial with the first deflecting roller, is guided further along the one slide bar, winds around a pulley located on the second servomotor, then extends along the other slide bar, is deflected around a fourth deflecting roller provided on the other side of the cradle and is guided along the guide means of the carriage to a fifth deflecting roller provided thereon by which it is deflected through 180° and is guided and deflected by a sixth deflecting roller provided on the cradle and coaxial with the fifth deflecting roller, and is guided further along the other slide bar and is also held fixed with respect to the apparatus at the other end on the side remote from the servomotor.

12. Mechanism according to claim 10 or claim 11 wherein the third servomotor is fixed with respect to the apparatus and the upward and downward motion is transmitted from the third servomotor to the dosing tube through a Bowden cable.

13. Mechanism according to claim 12 wherein a device for holding down a vessel is provided on the carriage so as to hold the sample vessel while the dosing tube is retracted and the holding down device is pivotally mounted and automatically deflected at the sample discharge station.

14. Mechanism for automatically supplying liquid samples from sample vessels to a measuring loop of a liquid chromatographic column substantially as described and as illustrated with reference to Figures 3, 4 and 5 or Figures 7 and 8 of the accompanying drawings.

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